Synthesis and Characterization of CuO-CdS Heterostructure

A Dissertation submitted in partial fulfilment of the requirements for the degree of

Integrated Master of Science
In
PHYSICS

By

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CERTIFICATE

This is to certify that, the work in the project report entitled **"*Synthesis and Characterization of CuO-CdS Heterostructure*"** submitted by **Priyabrata Mallick**, in partial fulfilment of the degree of Integrated Master of Science in Physics at National Institute of Technology, Rourkela; is carried out by him under my supervision and guidance. The above work is authentic and has not been submitted by anyone for fulfilment of any degree to the best of my knowledge.

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Date: **Priyabrata Mallick**

ABSTRACT

In this project CuO nanowires have been prepared by thermal oxidation of Cu foils and Cadmium Sulphide (CdS) nanoparticles were decorated on the surface of CuO nanowires by chemical vapor deposition (CVD) method. Prepared sample has been characterized by different characterization techniques such as X-Ray diffraction (XRD), Field Emission Scanning Electron Microscope (FESEM), Energy Dispersive Spectroscopy (EDS) and UV-Visible spectroscopy.

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1. General Introduction

1.1 Introduction to Nanotechnology

Nanotechnology has become a major area of interest for researchers from every discipline of science and technology. Nanomaterials are the basic component of the nanotechnology. Legal definition for nanomaterial was given by ISO (International Organization for Standardization) as material with any external dimension in nanoscale or any internal structure in nanoscale [3]. Basically, materials that come under length scale i.e. nanoscale (1-100 nm) are called nanomaterials. To get an idea how small a material is in nanoscale, we can compare to the diameter of an atom which varies from 0.1nm (1×10^{-10} m) to 0.5 nm (5×10^{-10} m). Nanotechnology has multidisciplinary application. Usages of nanotechnology does not confine in a particular discipline of science and technology. Manufacturing advance medical components, drugs, designing ultra-small electronic devices, fabricating stain resistant textiles, corrosion resistant material, fuel catalyst, cosmetics, clothing, packaging, disinfectants, food products and house hold appliances, the list for potential application of nanotechnology is infinite[1]. Nanotechnology is the technology of future.

There are different structures discovered for nanomaterials. On the basis of dimensions nanomaterials can be categorized into 1D (nanorods, nanowires and nanotubes) and 2D (thin films). Nanoparticles are special class nanomaterial in the context of dimensionality as they are categorized having zero dimensions. Apart from synthesizing in a laboratory nanomaterials can also be found abundantly in nature. Mostly biological systems feature nanostructures and nanomaterials. Silk of spider and spider-mite, lotus leaf, wings of butterfly are good examples of natural nanostructures and nanomaterials.[2] Artificial nanomaterial include fullerene, carbon nanotube, graphene, metal oxide nanowires like CuO nanowires, nanoparticles like cadmium selenide nanoparticles etc.

The main idea of nanotechnology and its potential was introduced by renowned physicist Richard Feynman in his famous talk at California institute of technology, entitled as “There is plenty of room at the bottom”, on December 29, 1959. The term nanotechnology was first used by Norio Taniguchi in 1974. After the invention of Scanning Tunneling Microscope (STM), it was possible to see individual atoms and manipulate them. STM was developed by Gerd Binning and Heinrich Rohrer in 1986 [43]. Atomic Force Microscope was also discovered in that year by Binning, Quate and Gerber. Also in the year of 1985 fullerene

was discovered by Harry Kroto, Richard Smalley and Robert Curl [44]. These new inventions helped the field of nanotechnology to grow in modern scientific era.

Due to very small size the properties of nanomaterials differ in important ways from properties of bulk materials and single atoms or molecules. So, controlled manipulation of size and shape of matter at nanoscale can produce structures, devices and systems with novel/superior characteristics or properties. Even the properties of bulk material can change dramatically with addition of nano-ingredients. All these extraordinary novel properties of nanomaterials are consequence of their small size. Properties and advantages of nanomaterials can be described as follows.

Surface of nanoparticles:

The most important consequence of small particle size is its huge surface area. It can be viewed as surface to volume ratio, which is indirectly proportional to the size i.e. diameter of the particle. So, if the size of the particle is very small then the surface area of the particle will be very large in comparison to its volume. This results in larger no of atoms on surface than that in volume. So, the surface of nanomaterials is much more reactive than surface of bulk material. This gives rise to the unique chemical properties of nanomaterials [4].

To understand this more elaborately we can say that atoms are present on the surface of the nanomaterial have less number of direct neighbours in comparison to the atoms in the bulk. As a result, particles with large number of atoms at the surface possess a low mean coordination number. This further makes those surface atoms more reactive in chemical reactions [5].

Quantum confinement:

This is the unique phenomenon that makes nanomaterials different than their bulk counterparts. When the particle size is comparable to the Bohr radius (a_0 = 0.053nm), the electron motion becomes confined. This means motion of the randomly moving electron is restrict in specific energy levels i.e. discreetness in the energy levels of electron. This effect widens the band gap. Band gap energy of the material is also increased due to this quantum confinement effect. The conduction band and conduction band splits into quantized energy levels [7, 8].

All the processes and techniques available for fabrication of nanomaterials can be divided into two categories: (i) Top-down approach and (ii) Bottom-up approach.

Top-down approach involves mostly mechanical processes like ball milling, cutting, and grinding. Techniques like etching and lithography i.e. photo lithography, ion beam lithography, e-beam lithography and X-ray lithography also comes under top-down approach. In top-down approach the bulk material is gradually broken to smaller components until nanoscale is reached. This approach is very useful for large scale synthesis of nanomaterials. But it has two major disadvantages. As mechanical processes are employed there is a very high chance of contamination in the prepared material. During processes like e-beam lithography and ion-beam lithography which involves very high energetic charge carriers there is high chance that the prepared material will have some defects. However modern top-down processes has reduced these shortcomings. Top-down approach implemented in manufacturing of computer hard drives, ultra-high quality mirrors etc [4][9][10].

Unlike top-down approach bottom-up approach does not involve application of mechanical tools rather it is purely chemical process like chemical bath deposition (CBD) and chemical vapor deposition (CVD), sol gel process. Atoms arrange themselves to form clusters particles smaller than nanomaterial size but larger than that of atoms. These clusters arrange themselves to fabricate nanoparticles and nanomaterials. This self-arrangement of atoms and molecule clusters to produce nanoparticle is termed as self-assembly. So we can say in bottom-up process atoms or molecules are used as building blocks to produce nanoparticles, nanotubes, nanowires, nanorods and thin films or layered structures. The major advantage of bottom-up approach is controllable synthesis of nanomaterials. By changing different parameters for chemical reaction, we can change characteristics of nanomaterials to get desired structures. Major disadvantage of bottom-up approach is large scale synthesis is not possible. Another shortcoming of bottom-up approach is, in some chemical reactions toxic byproducts are formed. Sometimes these byproducts are corrosive in nature. These byproducts are harmful for health and hazardous for environment.

1.2 Introduction to CVD

Chemical vapor deposition (CVD) is a bottom-up approach for synthesis of nanomaterials. CVD process can be defined as a process whereby a solid material is deposited onto the surface of a substrate through chemical reactions of gaseous species [11]. The depositing temperature and pressure are the critical parameters in this process. There are various

applications of CVD. Materials like Carbon-carbon, carbon-silicon carbide, silicon carbide-silicon carbide, composites, optical fibers, synthetic diamonds, sensors, optoelectronic devices, corrosion and high temperature resistant material coating can be done by CVD.

There are various advantages of CVD over other bottom-up approaches, which are:

CVD gives a good conformity in terms of uniform thickness of coating. This is called as conformal coverage. The coating can be done on complex structures. Interior and exterior of the substrate can be coated at the same time with uniform thickness of precursor material.

Chemical like halides and organo-metallic compounds can be used as precursor material in CVD. This gives a large variety of possible materials that can be synthesized by CVD. Materials of all three phase types (Solid, gas, liquid) can be used for coating. Ultra-high vacuum is not needed for CVD process. CVD is also useful for deposition of compounds into the multiple layers.

Disadvantage of CVD comes from its usages of different chemicals during the process of coating or material synthesis. Some of the reactants and by-products can be extremely toxic, explosive and corrosive in nature and must be handled with caution. This may cause health injuries as well as damage the environment. In order to reach suitable growth parameters many test runs are required. This makes CVD process very costly sometimes.

1.3 Introduction to heterostructure nanomaterials

Heterostructure consists of layers of two or more than two materials having different properties, combined to get novel and superior properties than its constituent material. Due to unique electrical, mechanical and optical properties, heterostructures have been irreplaceable components of semiconductor industry. They have applications in high speed electronics and optoelectronics. [12][13] Besides conventional semiconductors some 2D nanomaterials also provide good basic building blocks for heterostructure with unique electrical and optical properties. These materials include Graphene [14], hexagonal Boron nitride [15,16] and transition-metal di-chalcogenides (TMD) [17,18]

Various methods are implemented to fabricate heterostructures i.e. molecular beam epitaxy, CVD (Chemical Vapor Deposition), CBD (Chemical Bath Deposition) etc. Fabricated

heterostructure has different band gap than their parent semiconductor materials. This enables manufacturing of more advanced semiconductor devices like Field effect transistors [19].

1.4 Literature survey

In recent years one dimensional nanomaterials like nanowires, nanotubes and nanorods have become primary area of research due to their novel electrical, mechanical and optical properties. From these nanomaterials transition metal-oxide nanowires have become popular because of their extensive application in gas sensing[20][21], field emission[22], energy storage[23][24], catalysis[20], semiconductor devices[25], bio sensors[26], UV photo detector[27], photochemical water splitting[28] and solar cell[29][30].

In this context CuO is a promising candidate. It has promising use in semiconductor industry due to its narrow band gap which is 1.4 eV. CuO is p-type in nature [31]. Recent study shows that CuO is an antiferromagnetic material. Its magnetic moment per unit area has been found to be 0.60 μB [32]. CuO can also be used as base material for high-Tc superconductors [33][34]. From various techniques to grow CuO nanowires, thermal oxidation of Cu foils is the most simple. It is superior to other methods in a sense that it is low cost and catalyst free. There are two main reasons for Cu foil producing very high quality CuO nanowires on thermal oxidation. This is due to growth mechanism of CuO nanowires which can be described on the basis of unbalanced diffusion of metals and oxygen ions in both inward and outward direction[35][36].

Similarly Cadmium sulphide has also its usages as it is an n-type semiconductor material with band gap 2.42 eV and one of the best materials to fabricate solar cells [38]. So, it is one of the most suitable match for heterostructure with CuO. Besides CuO-CdS there are other heterostructures with enhanced photoresponse. For example ZnO/CdS heterostructure has enhanced photocatalytic properties [39]. ZnO/CdS heterostructure when prepared as core-shell can be applied in the field of solar energy conversion [40]. Similarly ZnO/CdSe heterostructure has also shown advanced photo catalytic activity [41].

Heterostructure of CuO and CdS have been prepared by chemical bath deposition method [42]. The main goal of this project is prepare CuO-CdS heterostructure by CVD process.

1.5 Definition of the problem

CVD has advantage over CBD in the context of current project goal which is to deposit CdS particles on the surface of CuO for fabrication of heterostructure. Instead of taking an chemical solution to deposit CdS, industrially synthesized powder of CdS can be taken as precursor and heated it in a CVD furnace to transform it into its gaseous phase. This gaseous CdS gets deposited on CuO substrate to form the heterostructure. So in CVD less amount of chemical is needed, this will reduce the overall cost of process. In CBD after coating the prepared sample has to be washed in NH_3. Sample has to be rinsed in deionized water and dried with nitrogen flow. This is done to avoid precipitation of cadmium hydroxide [42]. In case of CVD we do not have to go through all these complex steps. We can directly characterize the sample after deposition of CdS. So we can say CVD is way simpler process than CBD in context of preparation of CuO-CdS heterostructure.

2. Synthesis and Experimental Techniques

2.1 Preparation of CuO nanowires:

CuO nanowires were synthesized by thermal oxidation method. Copper foils of thickness 0.1mm and purity 99% were taken as substrates for CuO nanowire growth. Before subjected to annealing, Cu foils were cleaned to remove any kind of contaminating particles or any impurity layer. Extreme care and caution must be taken during the cleaning process of Cu foils as presence of any kind of contaminating particles on the surface of foils would reduce the quality of nanowires grown. Cleaning process was done in four steps. First Cu foils were cleaned in diluted Sulphuric acid (dil.H_2SO_4). In this step foils were dipped in diluted acid for 2 to 4 seconds. After cleaning with acid, Cu foils were subjected to sonication in distilled water for 10minutes and in absolute alcohol (Ethanol) for 10minutes**.**In final step Cu foils were rinsed with distilled water and dried in normal atmospheric condition. After drying Cu foils were subjected to thermal annealing in presence of air. For annealing process Cu foils were mounted in an alumina boat and put inside a tubular furnace for thermal oxidation process. Annealing was done at 400^0c for 6 hours. This is the optimum annealing condition for the well growth of the nanowires. After annealing furnace was let to be cooled down to normal temperature and CuO sample was retrieved from the furnace. A black and fragile sample was collected from the furnace and kept for further experiment and characterization.

2.2 Synthesis of CuO-CdS heterostructure nanomaterials

CuO-CdS core shell heterostructure nanomaterial was synthesized by chemical vapor deposition (CVD) method. In a typical process, , CdS powder (99.9% purity, Sigma Aldrich chemicals Co. Ltd.) was taken in the precursor holder made of alumina and placed inside the heating zone of the three zone CVD furnace at upstream of the gas flow. CuO nanowires grown on Cu foil were used as the substrate. CuO substrates were mounted in an alumina boat and placed inside the CVD furnace at downstream of gas flow. Nitrogen gas was used as the carrier gas for CVD process. The flow rate of nitrogen gas was kept at 1L/min. Temperatures set for three different heating zone were 400^0C, 500^0C, 500^0C respectively (in order from downstream to upstream of gas flow). The reaction was maintained for 30 minutes. After the completion of reaction, the samples were retrieved from the furnace and kept for further characterization.

2.3 X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD) technique is used for structural analysis of the material, as from XRD data we can study the atomic arrangement, lattice orientation, chemical bonds, their disorder and various other information regarding the material. Cu k_α radiation (λ=1.54056 A^0) is used for XRD because its wavelength is comparable to inter planar spacing (d) of the materials used for characterization. X-Ray diffraction satisfies the Brag's law of diffraction, which is;

$$2\ d\ Sin(\theta) = n\ \lambda$$

Where; θ = angle of diffraction

n = order of diffraction

λ = wavelength of incident X-ray radiation

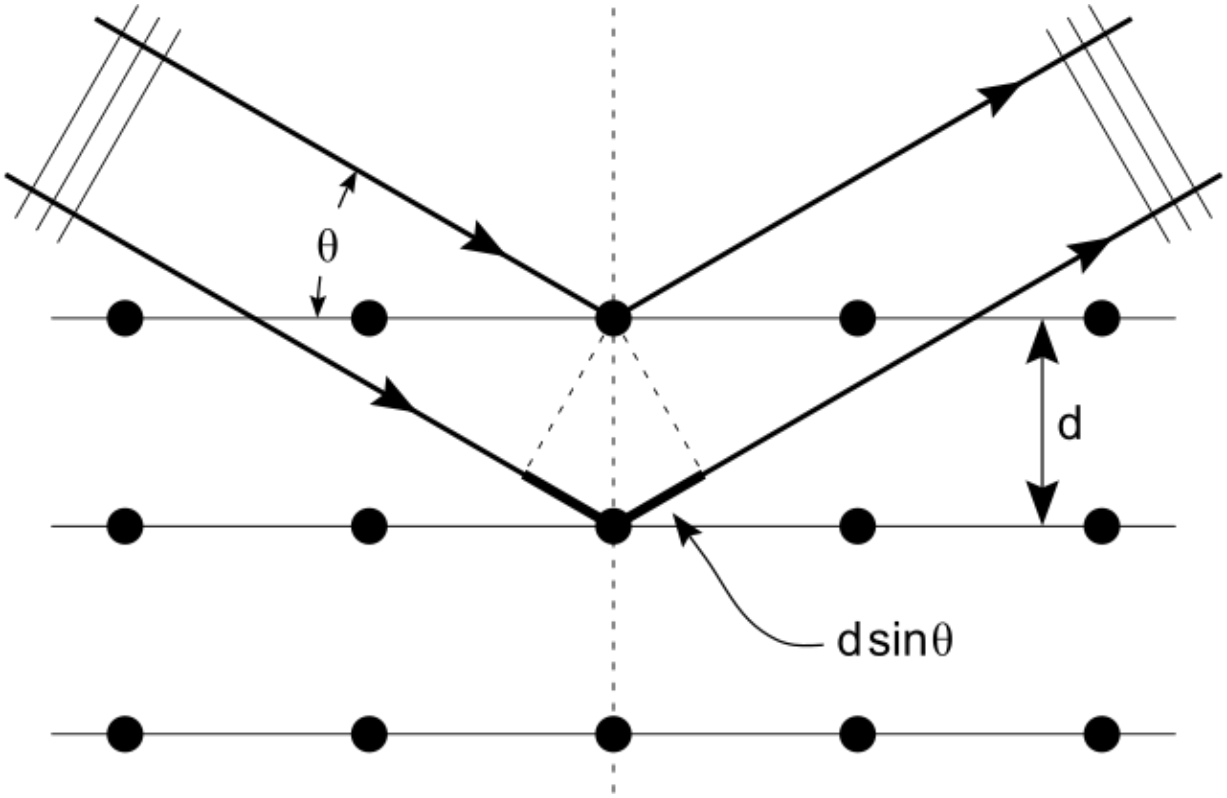


Figure [01] X-ray diffraction

2.4 Field Emission Scanning Electron Microscope (FESEM)

FESEM technique is used for analysis of surface morphology of the material. Beside topographical analysis compositional study of the sample can be done i.e. type of element present in the sample. FESEM require ultra-high vacuum to operate. Electrons are ejected from the source and accelerated through electrical field. Inside the vacuum column these ejected electrons i.e. primary electrons, are focused to produce a narrow beam. This beam of electrons is bombarded on the sample surface. These primary electrons knock out the electrons from the atoms of the sample. This process ionizes the sample. Knocked out electrons are called as secondary electrons. Some of the primary electrons scatter due to elastic collision and called as back scattered electrons. X-ray is also produced during the process of secondary electron production. Back scattered electrons are used to study topological contrast whereas secondary electrons are used for production of image of the specimen. Produced X-ray is used for techniques like energy dispersive spectroscopy to analyze the elemental composition of the material under study.

Advantage of FESEM on scanning electron microscope (SEM) is that it has better resolution. In FESEM field emission gun is used for electron generation instead of thermionic gun which is used in SEM. In case of FESEM sample is held at high negative potential (1-10kv) which facilitates an electric field at the tip shaped metallic sample in the field emission gun in order of 10^{10} v/m. This amount of electric field is more than enough for emission of electrons. In thermionic gun thermal energy is applied to generate electrons i.e. heating the filament inside the electron gun. Due to this reason FESEM can operate at low voltage (at 0.5kv) than SEM. Again field emission gun emits electrons from a smaller area than thermionic gun which enables it to focus the electron beam more perfectly. This results more clear and enhanced image even at low voltage. Spatial resolution in FESEM can go up to 1.5nm which is three to six times better than SEM.

Figure [02] FESEM machine

2.5 Energy Dispersive Spectroscopy (EDS)

Energy dispersive spectroscopy is a special characterization technique which analyses the elemental composition of the material of the sample studied in SEM and FESEM. EDS analysis can determine impurity type and plot them with respect to concentration in the sample. It can be used as alternative for confirmation of synthesized material. Only disadvantage of EDS is it can't detect elements with atomic weight less than that of carbon.

In SEM, electron beam which is focused on the sample generates X-ray fluorescence due to the collision with atoms in its path. Each element can be characterized from the energy spectrum of the X-ray produced by it due to the interaction with bombarding electrons. Analysis system for energy dispersive spectroscopy collects these photons of produced X-ray and plots their intensity i.e. counts per second, according to their energy spectrum. Identification of the elements present is done by matching the peaks of their energy distribution. This matching process is automatically done by the EDS system and output is displayed in the form a plot between voltage of bombarding electron in X-axis and number of emitted photons as counts per second in Y-axis.

2.6 UV-Vis Spectroscopy

UV-Visible spectrum ranges from 200nm to 800nm. If a material is active towards the radiation in this range then it can be analyzed by using a UV-Visible spectrometer. A material is called active towards a certain range of wavelength if it absorbs or emits radiation in that range of wavelength in electromagnetic spectrum. In UV-Visible spectrometer this wide range (200-800 nm) of electromagnetic radiation is produced by combination of two lamps. For UV part of spectrum (100-400 nm) a deuterium lamp is used. Similarly a halogen lamp is used to produce radiation of visible spectra (390-700nm). Combined output of these two lamps is focused through a diffraction grating to get the desired UV-Visible spectrum.

Two different containers are used for testing of sample. One is for solution of sample in a suitable solvent and other container holds only solvent. First container is referred as sample cell and the later one as reference cell. The most important characteristics of the solvent is that it shouldn't absorb any significant amount of incident radiation, otherwise it will give rise to errors in calculation. These containers are made of glass or quartz. Incident light passes through these containers and collected by detector which transforms the incoming UV-Visible radiation into the current. Magnitude of this current is directly proportional to the

intensity of the radiation that is incident upon the sample cell. Intensity of radiation that passes through the reference cell is measured as I_0. Similarly, I is the measurement of intensity of radiation that passes through sample cell. Using this data absorbance of the sample can be calculated by using the formula;

$$\mathbf{A = \log_{10} (I_0/I)}$$

Absorbance ranges from 0 to 1. Zero absorbance indicates that no radiation of particular wavelength has been absorbed. Similarly an absorbance of one means 90% of incident radiation has been absorbed by the sample. Absorbance data is plotted against the wavelength to show the absorbance peak of the sample. Analyzing this plot we can know at which wavelength the sample absorbs more or less amount of UV-Visible radiation. Matching the absorption pattern with that of known chemical compounds we can determine type of compound and functional group present in the sample. In UV-Visible spectroscopy Beer-Lambert law is widely used to calculate molar absorptivity, concentration of the sample. It is given by; $\mathbf{A = \varepsilon\, l\, c}$

Where A = Absorbance

ε = molar absorptivity of the solution

l = length of the solution the light passes through

c = concentration of the solution

From UV-Visible analysis we can also plot Tauc graph to get band gap of the material using formula; $\mathbf{\alpha\, h\, \nu = A\, (h\, \nu - E_g)^n}$

where α = Absorption coefficient.

ν = Frequency of incident radiation.

h = Planck's constant.

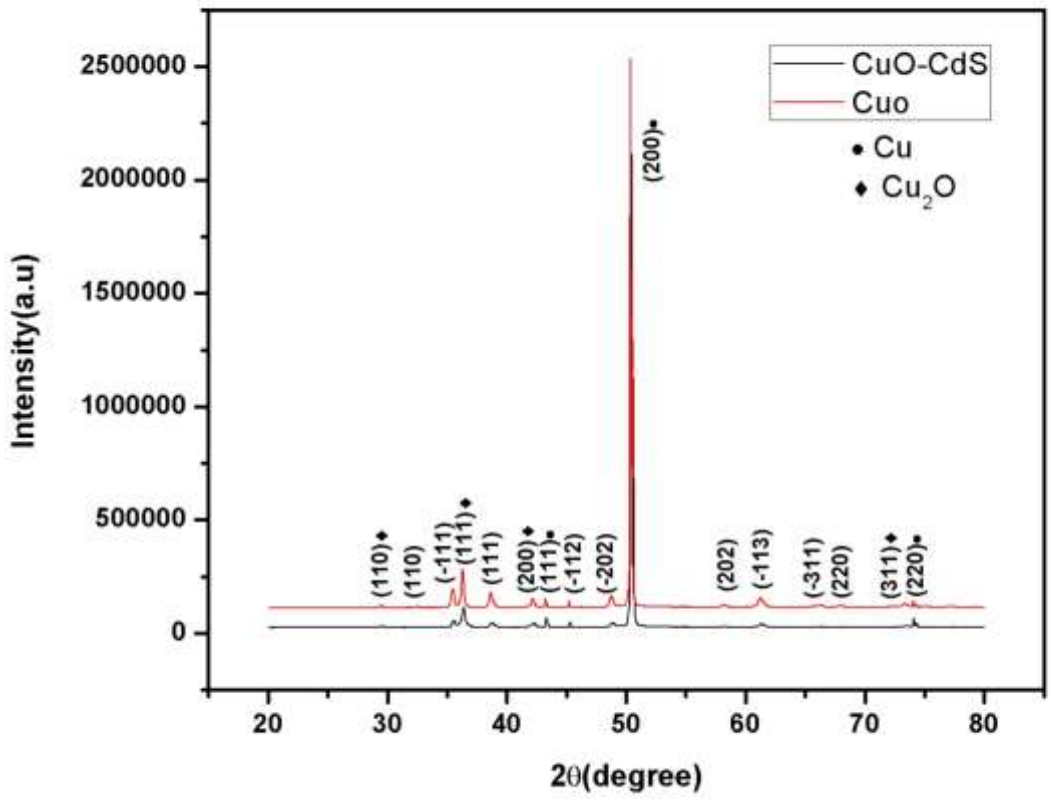
E_g = Band gap of the material.

n = order of transition, it is equal to ½ for direct allowed transition.

A = Absorbance

3. Result & discussion

3.1 X-ray Diffraction

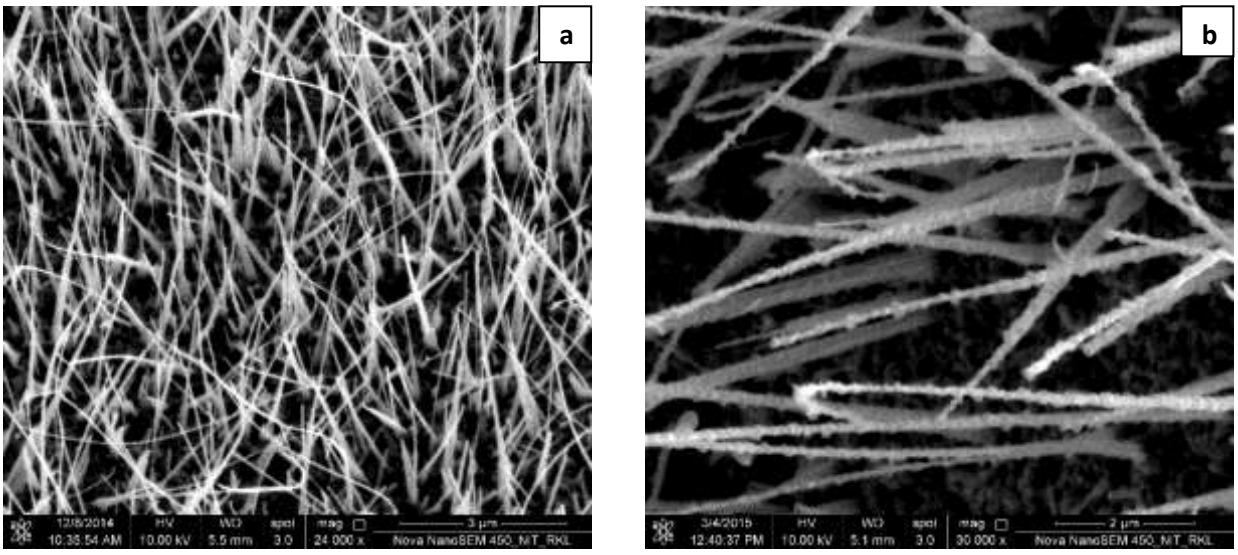


Figure[03]: XRD pattern of CuO nanowires and CuO-CdS heterostructured nanomaterials

Figure[03] shows XRD pattern for CuO nanowire and CuO-CdS heterostructure. From the XRD pattern of CuO nanowire it has been confirmed that the nanowires are highly crystalline in nature. However the major peak (220) belongs to Cu. This is because Cu foil has been taken as substrate for the preparation of CuO nanowires. There are few Cu2O phase seen in the pattern. Furthermore, from the XRD pattern it is revealed that the CuO nanowires are polycrystalline. The pattern is well matched with JCPDS numbers as 80-0076 (CuO), 05-0667 (Cu2O), 02-1225 (Cu).

After the synthesis of CuO-CdS heterostructure, it is seen that the intensity of the peaks have been reduced and few peaks have been disappeared from the pattern. It may be due to the coating of CdS nanocrystallites onto the surface of CuO nanowires.

3.2 Field Emission Scanning Electron Microscopy

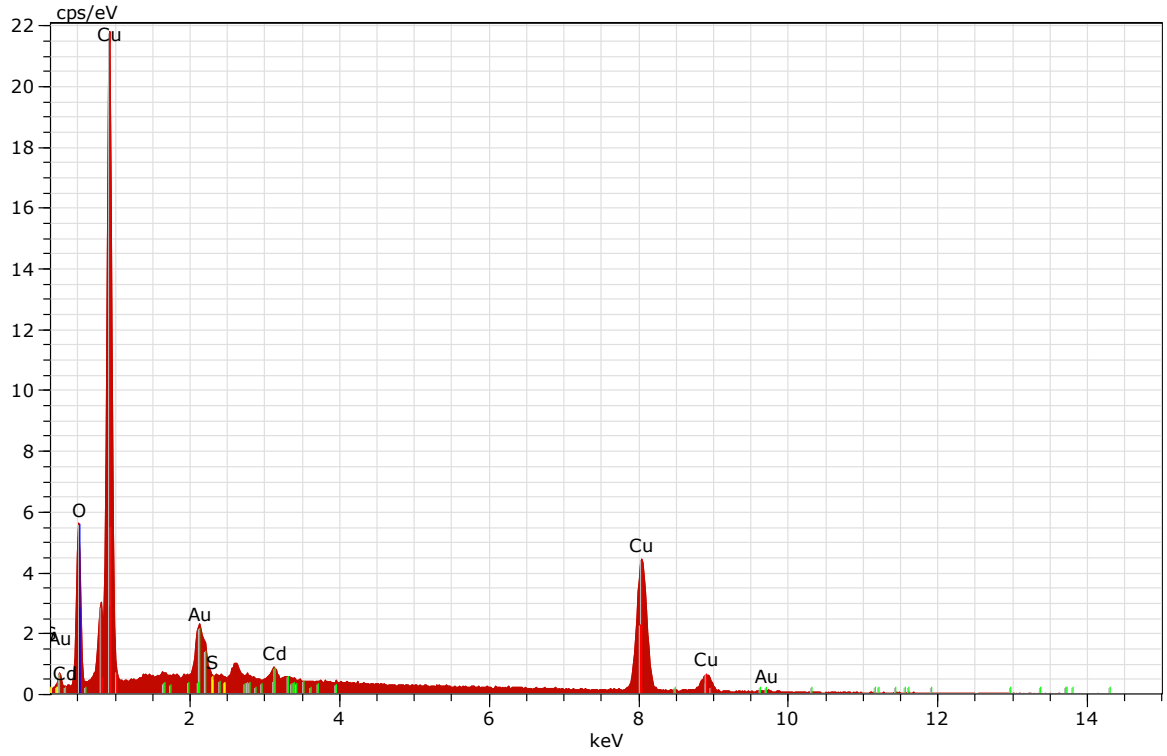


Figure[04] (a)FESEM image of CuO nanowires, (b) FESEM image of CuO-CdS heterostructure

Figure [04](a) shows FESEM images of CuO nanowires and CuO-CdS heterostructure nanomaterials. From FESEM image (a), it confirms the formation of CuO nanowires which has been grown on the Cu foil. The CuO nanowires have grown densely. Most of the CuO have grown in nanowire structure that means the diameter is same across the length. However few nano-needle shaped CuO have been formed i.e. diameter decreases as we go from bottom to top. The surface of the CuO nanowires is seen to be smooth. The average length and diameter of the nanowires is found to be 4.8μm and 0.05μm respectively. However few nanowires have seen to be grown very long.

Figure [4](b) shows the FESEM image of CuO-CdS heterostructure nanomaterial. From the image it confirms the decoration of CdS onto the surface of CuO nanowires. The surfaces of the nanowires are seen to be rough after deposition of CdS particles. The average length and diameter of CdS nanoparticle decorated CuO nanowires is found to be 4.9μm and 0.17μm. Since, few CuO nanowires are found to be nano-needle shaped, some of the CdS nanoparticle decorated CuO nanowires are found to be in needle shape

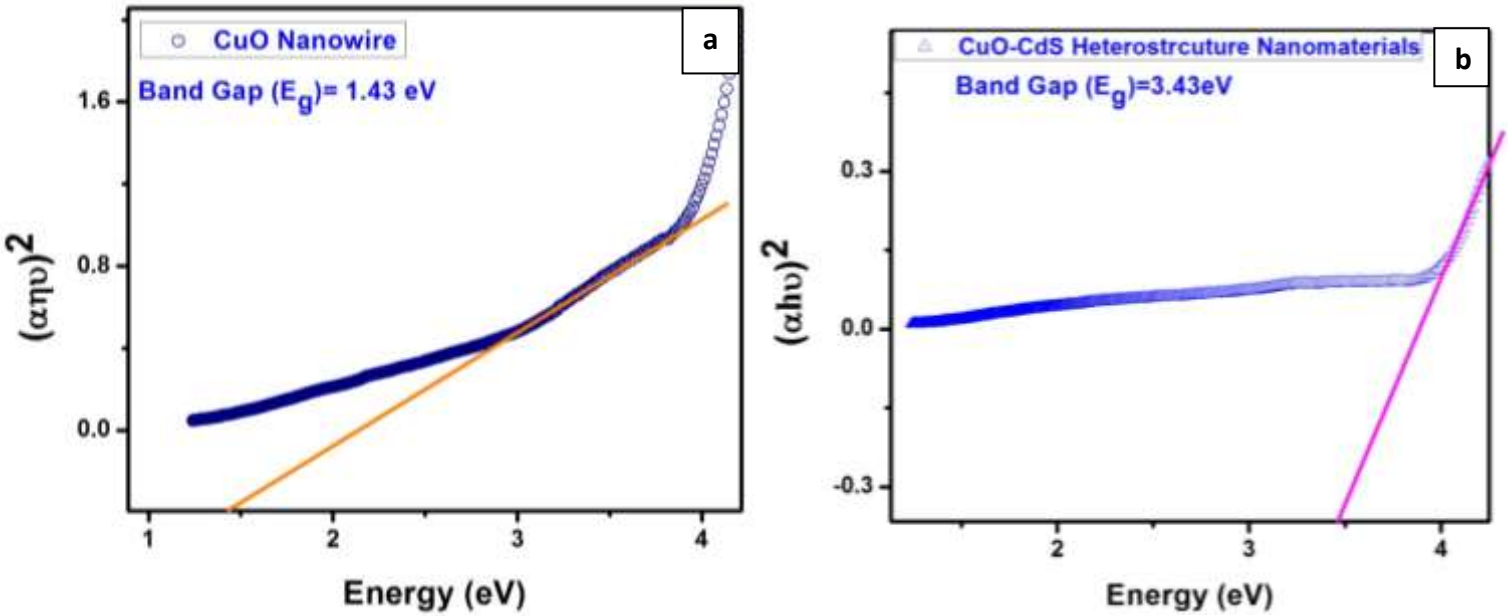
3.3 Energy Dispersive Spectroscopy



Figure[05] EDS spectra of CuO-CdS heterostructure

From figure [05] it is confirmed that copper, oxygen, Cadmium, Sulphur are present in the sample. Presence of gold is due to the coating done before mounting the sample in FESEM, in order to make the surface of the sample conductive. Presence of all the required elements i.e. Copper, cadmium, Sulphur and oxygen ensures the formation of CuO-CdS heterostructure.

3.4 UV-Vis Spectroscopy



Tauc plot of (a) CuO nanowires, (b) CuO-CdS heterostructure.

Figures [06](a) and [06](b) shows the Tauc plot of CuO nanowires and CdS nanoparticle decorated CuO nanowires. The band gap of CuO nanowires is found to be 1.43eV. After the deposition of CdS onto the surface of CuO nanowires the band gap has been changed to 3.43eV. Hence the band gap can be tuned by incorporating CdS nanoparticles onto the surface of CuO nanowires by changing the synthesis parameters.

Conclusion

CuO nanowires were successfully synthesized by thermal oxidation of Cu foils. CdS-CuO heterostructure was prepared by chemical vapor deposition (CVD) technique using CuO nanowires as substrates and CdS as precursor. The decoration of CdS crystals onto the surface of CuO nanowire is confirmed from FESEM micrograph. From the analysis of energy dispersive spectroscopy (EDS), it is confirmed that all the elements that should be present for formation of CuO-CdS heterostructure are there in the sample. Using the data from UV-Visible spectra the Tauc plot has been plotted for both CuO nanowires and CuO-CdS heterostructure. From this plot band gaps of CuO nanowire and CuO-CdS heterostructure were found to be 1.43 eV and 3.43 eV respectively.

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